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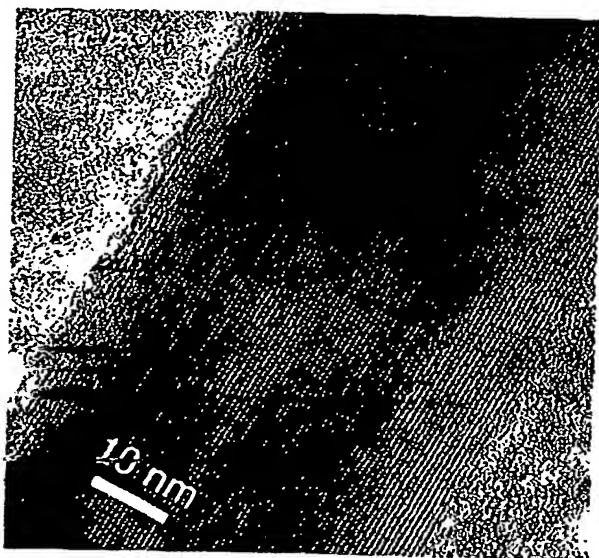
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[Continued on next page]

(54) Title: PREPARATION OF METAL CHALCOGENIDES FROM REACTIONS OF METAL COMPOUNDS AND CHALCOGEN



(57) Abstract: A method of preparing metal chalcogenides from elemental metal or metal compounds has the following steps: providing at least one chalcogen; providing at least one element from periodic table groups 13-15; providing at least one elemental metal or metal compound; and combining and heating the chalcogen, the group 13-15 element, and the metal or metal compound at sufficient time and temperature to form a metal chalcogenide. Methods of preparing metal sulfides and polysulfides from metal oxides; a kit comprising boron and a chalcogen; a method of preparing ultralong TaS₃ nanowires from tantalum metal; a battery comprising TaS₃; a method of preparing semiconducting chalcogenide nanoparticles and controlling sizes and morphologies in solution; methods of: preparing CdSe nanocrystals and controlling their size/preparing CdSe nanocrystals of controlled size; a method of preparing metal chalcogenide nanocrystals of controlled size; and a method of functionalizing the surface of semiconducting chalcogenide nanoparticles.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US04/02929

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01B 17/00; C01B 19/00; C01B 19/04; C01F 17/00
US CL : 423/263, 266, 509, 561.1; 976/DIG. 1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 423/263, 266, 275, 508, 509, 511, 561.1, 659; 976/DIG. 1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
USPTO EAST Database (accesses USPAT, USPGPUB, EPO, JPO, DERWENT, and IBM_TDB databases)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,778,539A (KUBO et al.) 18 October 1988 (18.10.1988), column 2, lines 12-23, Examples 1-3 and 5-7 in columns 4-9.	1-3
X	FELDMAN et al. Bulk Synthesis of Inorganic Fullerene-like MS2 (M = Mo, W) from the Respective Trioxides and the Reaction Mechanism. J. Am. Chem. Soc. 1996, Vol. 118, pages 5362-5367, especially title, last full paragraph of column 2 on p. 5363, paragraph bridging pp. 5364 - 5365.	1, 3 and 4
X	US 3,770,422 A (DARNELL et al.) 06 November 1973 (06.11.1973), abstract, column 4, lines 28-31 and 33-37, Example 5 in column 11.	1 and 3
X	Chemical Abstract Accession No. 2000:864660 (QIAN et al.) 12 December 2000 (12.12.2000), Preparation of nanometer compounds of sulfur family or phosphorous family.	20
Y	Title and abstract.	20
A	US 3,009,977 A (HOUSTON) 21 November 1961 (21.11.1961), entire document in general.	1-4
A	JP 1-305806 A (MITSUBISHI PETROCHEMICAL CO., LTD) 11 December 1989 (11.12.1989), entire document in general.	20

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	"T"
"A" document defining the general state of the art which is not considered to be of particular relevance	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"B" earlier application or patent published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Continuation Sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.: 1-4 and 20
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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BOX III. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

The Groups are as follows:

Group I, claims 1-4, drawn to a method of preparing metal chalcogenides from elemental metal and metal compounds, the method comprising providing: a. at least one chalcogen; b. at least one element from periodic table groups 13-15; c. at least one elemental metal or metal compound; and combining and heating a., b. and c. at sufficient time and temperature to form a metal chalcogenide.

Group II, claims 5-8 and 13-19, drawn to methods of preparing metal sulfides and polysulfides from metal oxides, based upon the following steps: a. providing boron, pure sulfur, and pure metal oxide powder; b. placing the boron and sulfur in a first tube; c. placing the metal oxide powder in a second tube; d. placing the two tubes into a larger container; e. evacuating and sealing the container; f. gradually heating the container to a specific temperature range; and g. keeping the container at that temperature until little or no boron remains.

Group III, claim 9, drawn to a "kit" comprising boron and a chalcogen (all other components being optional).

Group IV, claims 10-11, drawn to a method of preparing ultralong TaS₃ nanowires from tantalum metal, the method comprising: a. providing at least one piece of tantalum; b. providing and placing boron and sulfur in a first tube; c. placing the tantalum piece in a second tube; d. placing the two tubes into a container; e. evacuating and sealing the container; f. gradually heating the container to a specific temperature range; and g. cooling the container to room temperature.

Group V, claim 12, drawn to a battery comprising TaS₃ as a "positive anode" (presumably, a "positive electrode" (i.e., a cathode), based upon p. 19, the last sentence, of the description).

Group VI, claim 20, drawn to a method of preparing semiconducting chalcogenide nanoparticles and controlling sizes and morphologies in solution, the method comprising providing: a. at least one metal compound; b. at least one chalcogen; c. at least one element selected from "the periodic table groups 13-15 (B, Al, Ga, In, Si, Ge, Pb, P, As, Sb and Bi)"; and mixing a., b. and c. in a solution at sufficient temperature and time to produce precipitate.

Group VII, claims 21-28 and 34, drawn to methods of: preparing CdSe nanocrystals and controlling their size/preparing CdSe nanocrystals of controlled size, based upon the following steps: providing specific reactants in amine solvents; mixing; and heating the resulting solution to a temperature in the range of about 50 to 250 °C for selected reaction periods, whereby the CdSe nanocrystals form and their size varies with the temperature and reaction period.

Group VIII, claims 29-31, drawn to a method of preparing metal chalcogenide nanocrystals of controlled size, based upon the following steps: providing specific reactants in amine solvents; mixing; and heating the resulting solution to 100 °C via

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microwave irradiation for 40 seconds, whereby metal chalcogenide nanocrystals of controlled size form, wherein the metal chalcogenide is selected from the group consisting of CdS, ZnSe and PbSe.

Group IX, claims 32-33, drawn to a method of functionalizing the surface of semiconducting chalcogenide nanoparticles, the method comprising: providing a. at least one metal compound; b. providing one chalcogenide having a cation selected from "groups 13 -15 (B, Al, Ga, In, Si, Ge, Pb, P, As, Sb and Bi)"; c. dissolving a. in a first solution; d. dissolving b. in a second solution; e. providing and dissolving a functional capping agent in at least one of the first or second solutions; f. combining all solutions; and g. maintaining the resultant solution at a proper temperature for an appropriate time.

The inventions listed as Groups I-IX do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The inventions listed as Groups I-IV and VI-IX lack the same or corresponding technical features discussed supra. That is:

- the special technical feature of Group I relates to heating and combining the reactants listed as a., b. and c. in claim 1 at sufficient time and temperature, so as to prepare a metal chalcogenide;
- the special technical feature of Group II relates to the placement of boron, pure sulfur and pure metal oxide powder in various tubes which are evacuated, sealed, heated and aged at a specific temperature, so as to prepare metal sulfides and polysulfides from metal oxides;
- the special technical feature of Group III relates to the combination of boron and a chalcogen in "kit" form;
- the special technical feature of Group IV relates to the placement of a piece of tantalum, boron and sulfur in various tubes which are evacuated, sealed, heated and cooled to room temperature, so as to prepare ultralong tantalum trisulfide nanowires from tantalum metal;
- the special technical feature of Group VI relates to mixing the reactants listed as a., b. and c. in claim 20 in a solution at sufficient temperature and time to produce precipitate, in a method of preparing semiconducting chalcogenide nanoparticles and controlling sizes and morphologies in solution.
- the special technical feature of Group VII relates to providing specific reactants in amine solvents; mixing; and heating the resulting solution to a temperature in the range of about 50 to 250 °C for selected reaction periods, so as to prepare CdSe nanocrystals whereby their size varies with the temperature and reaction period.
- the special technical feature of Group VIII relates to providing specific reactants in amine solvents; mixing; and heating the resulting solution to 100 °C via microwave irradiation for 40 seconds, so as to prepare metal chalcogenide nanocrystals of controlled size, wherein the metal chalcogenide is selected from the group consisting of CdS, ZnSe and PbSe.
- the special technical feature of Group IX relates to providing a. at least one metal compound; providing b. one chalcogenide having a cation selected from "groups 13 -15 (B, Al, Ga, In, Si, Ge, Pb, P, As, Sb and Bi)"; c. dissolving a. in a first solution; d. dissolving b. in a second solution; e. providing and dissolving a functional capping agent in at least one of the first or second solutions; f. combining all solutions; and g. maintaining the resultant solution at a proper temperature for an appropriate time, in a method of functionalizing the surface of semiconducting chalcogenide nanoparticles.

With respect to Group V:

-Claim 12 of Group V is at least obvious over, if not anticipated by, US 3 864 167 A (BROADHEAD ET AL.) 04 February 1975. See claim 1 in column 5, noting that the positive electrode material may specifically be tantalum trisulfide (see also col. 4, lines 38-39). Consequently, the special technical feature of Group V-which is clearly different than that from Groups I-IV and VI-IX discussed supra-does not provide a contribution over the prior art, and unity of invention is lacking.

In addition:

This application contains claims directed to more than one species of one or more of the above generic inventions. These species are deemed to lack unity of invention, because they are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for more than one species to be examined, the appropriate additional examination fees must be paid.

The species are as follows:

If Group II is elected:

Embodiments wherein:

1. the metal sulfide is NdS₂ and the metal oxide is Nd₂O₃;
2. the metal sulfide is In₂S₃ and the metal oxide is In₂O₃;
3. the metal sulfide is PbS and the metal oxide is PbO;
4. the metal sulfide is KInS₂ and the metal oxide is In₂O₃, supplemented with KCO₃;
5. the metal sulfide is NaInS₂ and the metal oxide is In₂O₃, supplemented with NaF; or
6. the metal sulfide is NaBiS₂ and the metal oxide is NaBiO₃.

With respect to Group II, the claims are deemed to correspond to the species listed above in the following manner:

1. Claim 6.
2. Claim 13.
3. Claim 14.

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4. Claim 16.
5. Claim 17.
6. Claim 19.

With respect to Group II, the following claims are generic: claims 5, 7 and 8.

If Group VIII is elected:

Embodiments wherein:

1. the metal chalcogenide nanocrystals are CdS;
2. the metal chalcogenide nanocrystals are ZnSe; or
3. the metal chalcogenide nanocrystals are PbSe.

With respect to Group VIII, the claims are deemed to correspond to the species listed above in the following manner:

1. Claim 29.
2. Claim 30.
3. Claim 31.

With respect to Group VIII, the following claims are generic: none.

The species listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons:

With respect to both Group II and Group VIII, pursuant to PCT Rule 13.2 and PCT Administrative Instructions, Annex B, Part 1 (f)(I)(B)(2), the species within both groups are not art recognized equivalents.